HYDROGEN DONOR EFFECT
ON POLYMER DEGRADATION IN SOLUTION

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ABSTRACT

An important effect in the degradation of solubilized polymers is the influence of the solvent on the degradation rate. Depending on the particular polymer, hydrogen (H-)donors can increase, decrease, or have no effect on degradation rate. We experimentally investigated the effect of H-donor 6-hydroxy tetralin on polystyrene degradation. In this case the rate decreases with increasing H-donor concentration. Mathematical expressions for the degradation rate parameters were obtained by applying continuous-distribution kinetics to the MWD of the reacting polymer. A model was developed for radical mechanisms based on the Rice-Herzfeld chain-reaction concept with the elementary steps of initiation, depropagation, H-abstraction and termination. The model accounted for the varied effects of the H-donor on polymer degradation.

INTRODUCTION

Thermochemical recycling of polymers as either fuel or feedstock has been receiving growing attention in recent years. The degradation of polystyrene has been extensively investigated by pyrolysis (Cameron and MacCallum, 1967) though the mechanism and kinetics of polystyrene degradation remain subjects of discussion (McNeill et al., 1990). Degradation of polymers in solution was proposed to counter the problems of low heat transfer rates and high viscosity of the melting polymer commonly encountered in polymer recycling by pyrolysis (Sato et al., 1990). The degradation of polystyrene (Murakata et al., 1993a; Madras et al., 1996), poly(styrene-allyl alcohol) (Wang et al., 1995), poly(methyl methacrylate) (Madras et al., 1996a), poly (p-methyl styrene) (Murakata et al., 1993b) and poly (α-methyl styrene) (Madras et al., 1996b) in solution have been investigated. By pyrolysis, we mean the thermal decomposition of a solid material at high temperatures to yield gas and liquid products of low MW. Thermolysis of polymers in solution produces a mixture of solubilized products. In either case, the decomposition yields a product mixture that can often be described as a continuous function of MW. The time evolution of the molecular weight distribution (MWD) can be examined by continuous-distribution kinetics to determine the rate parameters and provide insights into the decomposition mechanisms.

The solvent effect for polystyrene thermal degradation was investigated by Sato et al. (1990). The conversion of polystyrene to low molecular weight products decreased with the increase of the H-donating ability of the solvents. The study, however, did not determine degradation rate coefficients. Madras et al. (1995) found that tetralin enhanced the rate of degradation of poly(styrene-allyl alcohol). Rate coefficients were determined as a function of tetralin concentration and temperature. Madras et al. (1996a) found that tetralin had no effect on the degradation of poly(α-methyl styrene). These studies indicate the varied effect of the H-donor on polymer decomposition. Though there have been several experimental studies on H-donor solvents, an overall theory for the mechanism is not available.

EXPERIMENTS

The HPLC (Hewlett-Packard 1050) system consists of a 100 mL sample loop, a gradient pump, and an on-line variable wavelength ultraviolet (UV) detector. Three PLgel columns (Polymer Lab Inc.) (300 mm x 7.5 mm) packed with cross-linked poly(styrene-divinyl benzene) with pore sizes of 100, 500, and 10^4 Å are used in series. Tetrahydrofuran (HPLC grade, Fisher Chemicals) was pumped at a constant flow rate of 1.00 mL/min. Narrow MW polystyrene

standards of MW 162 to 0.93 million (Polymer Lab and Aldrich Chemicals) were used to obtain the calibration curve of retention time versus MW.

The thermal decomposition of polystyrene in mineral oil was conducted in a 100 mL flask equipped with a reflux condenser to ensure the condensation and retention of volatiles. A 60 mL volume of mineral oil (Fisher Chemicals) was heated to 275 °C, and various amounts (0 - 0.60 g) of the H-donor, 6-hydroxy tetralin (Aldrich Chemicals), and 0.12 g of monodisperse polystyrene (MW = 110,000) (Aldrich Chemicals) were added. The temperature of the solution was measured with a Type K thermocouple (Fisher Chemicals) and controlled within ± 3 °C using a Thermolyne 45500 power controller. Samples of 1.0 mL were taken at 15 minute intervals and dissolved in 1.0 mL of tetrahydrofuran (HPLC grade, Fisher Chemicals). An aliquot (100 μL) of this solution was injected into the HPLC-GPC system to obtain the chromatograph, which was converted to MWD with the calibration curve. Because the mineral oil is UV invisible, its MWD was determined by a refractive index (RI) detector. No change in the MWD of mineral oil was observed when the oil was heated for 3 hours at 275 °C without polystyrene.

THEORETICAL MODEL

According to the Rice-Herzfeld mechanism, polymers can react by transforming their structure without change in MW, e.g., by H-abstraction or isomerization. They can also undergo chain scission to form lower MW products, or undergo addition reactions yielding higher MW products. Chain scission can occur either at the chain-end yielding a specific product, or at a random position along the chain yielding a range of lower MW products. The radicals formed by H-abstraction or chain scission are usually influenced by the presence of the H-donor.

We propose continuous-distribution mass (population) balances for the various steps involved in the radical mechanism. The rate coefficients are assumed to be independent of MW, a reasonable assumption at low conversions (Madras et al., 1997). The integrodifferential equations obtained from the mass balances were solved for MW moments. In general, the moments are governed by coupled ordinary differential equations that can be solved numerically. In the present treatment, two common assumptions are made that allow the equations to be solved analytically. The long-chain approximation (LCA) (Nigam et al., 1994; Gavalas, 1966) is valid when initiation and termination events are infrequent compared to the hydrogen-abstraction and propagation-depropagation events. Thus the initiation-termination rates are assumed to be negligible. The quasi-stationary state approximation (QSSA) applies when radical concentrations are extremely small and their rates of change are negligible.

Polymer degradation in some circumstances can occur solely by random chain scission. We represent the chemical species of the reacting polymer, and the radicals as $P(x)$ and $R^*(x)$ and their MWDs as $p(x,t)$ and $r(x,t)$, respectively, where x represents the continuous variable, MW. Since the polymer reactants and random scission products are not distinguished in the continuous distribution model, a single MWD, $p(x,t)$, represents the polymer mixture at any time, t. The initiation-termination reactions are ignored, according to the LCA. The reversible H-abstraction process is simplified to

$$P(x) \overset{k_b}{\underset{k_H}{\Leftrightarrow}} R^*(x) \tag{1}$$

The random-scission chain reaction is

$$R^*(x) \overset{k_b}{\to} P(x') + R^*(x-x') \tag{2}$$

The reversible H-donor reactions are

$$P(x) + D^{\bullet} \overset{k_d}{\underset{k_D}{\Leftrightarrow}} R^{\bullet}(x) + D \tag{3}$$

where D and $D^{\bullet}$ represent the H-donor and its dehydrogenated form, respectively. Because the MW of $P(x)$ and $R^{\bullet}(x)$ differ only by the atomic weight of hydrogen, we consider their MWs are the same.

The population balance equations for the polymer MWD, $p(x,t)$, and for the radical MWD, $r(x,t)$, are formulated and solved by the moment method (McCoy and Madras, 1997). Both the LCA and the QSSA are applied to obtain the zeroth moment expression in terms of the initial condition, $p^{(0)}(t=0) = p_0^{(0)}$,

$$p^{(0)}(t) = p_0^{(0)} \exp(k_r t) \tag{4}$$

and a plot of $\ln(p^{(0)}/p_0^{(0)})$ should be linear in time with slope k_r,

$$k_r = k_b (k_h + k_d C)/(k_H + k_D C) \tag{5}$$

This equation, showing how the degradation rate coefficient depends on H-donor concentration, C, is plotted in Figure 1 for several special cases.

Polymers like poly(α-methyl styrene) undergo degradation by chain-end scission yielding monomers and other low-MW specific products, $Q_s(x_s)$. The chain-end scission reaction is

$$P(x) \overset{k_{fs}}{\rightarrow} R_e^{\bullet}(x) + R_e^{\bullet}(x - x') \tag{6}$$

H-abstraction by the chain-end radical is considered reversible,

$$P(x) \overset{k_{he}}{\underset{k_{He}}{\Leftrightarrow}} R_e^{\bullet}(x) \tag{7}$$

The chain-end radical, $R_e^{\bullet}(x)$, can also undergo radical isomerization to form a specific radical, $R_s^{\bullet}(x)$, via a cyclic transition state,

$$R_e^{\bullet}(x) \overset{k_{ih}}{\underset{k_{iH}}{\Leftrightarrow}} R_s^{\bullet}(x) \tag{8}$$

The reversible, propagation-depropagation reactions whereby a specific radical yields a specific product and a chain-end radical is

$$R_s^{\bullet}(x) \overset{k_{bs}}{\underset{k_{as}}{\Leftrightarrow}} Q_s(x_s) + R_e^{\bullet}(x-x_s) \tag{9}$$

The reactions of the H-donor expressed in terms of D, the hydrogenated and $D^{\bullet}$, the dehydrogenated forms of the donor, are

$$P(x) + D^{\bullet} \overset{k_{de}}{\underset{k_{De}}{\Leftrightarrow}} R_e^{\bullet}(x) + D \tag{10}$$

Applying the LCA and QSSA to the population balance equations yields for the specific product,

$$q_s^{(0)}(t) = k_s p_0^{(0)} t \tag{11}$$

where

$$k_s = (k_{he} + k_{de}C) k_{bs} k_{ih} / ((k_{bs} + k_{iH})(k_{He} + k_{De}C)) \tag{12}$$

This is a key result for chain-end scission influenced by H-donor concentration, C, and is similar to eq. 5 for random chain scission. A plot of $q_s^{(0)}(t)/p_0^{(0)}$ versus time would be linear with a slope k_s, which depends on C.

DISCUSSION

The random-scission degradation rate coefficient, k_r, was determined from the experimental data by analyzing the time dependence of the polystyrene MWDs. The graphs of

$p_{tot}^{(0)}/p_{tot0}^{(0)}$ versus time for various H-donor concentrations were linear after 45 minutes. For times less than 45 minutes, scission of weak links causes a rapid increase in the molar concentration (Stivala et al., 1983; Madras et al., 1997; Chiantore et al., 1981). The initial molar concentration of the strong links in polystyrene, $p_0^{(0)}$, is determined from the intercept of the regressed line of the $p_{tot}^{(0)}/p_{tot0}^{(0)}$ data for $t \geq 45$ minutes. The slopes, corresponding to the rate coefficient for random scission, k_r, are determined from the plot of $\ln (p^{(0)}/p_0^{(0)})$ versus time. The rate coefficient decreases with increasing H-donor (6-hydroxy tetralin) concentration (Figure 2). This behavior is consistent with eq. 5 when $k_d C \ll k_h$ (Figure 1). This behavior is also observed for the polystyrene degradation in the presence of tetralin (Sato et al., 1990).

When $k_h \ll k_d C$, the rate coefficient has a first-order dependence at low H-donor concentrations and a zero-order dependence at high H-donor concentrations. This has been experimentally observed for poly(styrene-allyl alcohol) degradation in the presence of tetralin at 150 °C (Madras et al., 1995). When $k_d C \ll k_h$ and $k_D C \ll k_H$, the rate coefficient is independent of the H-donor concentration. This is consistent with poly(α-methyl styrene) degradation in the presence of H-donor solvents.

For chain-end scission, the effect of H-donor concentration is qualitatively similar to that in Figure 1. For the chain-end scission rates for the degradation of poly(styrene allyl-alcohol) in the presence of tetralin at 150 °C (Madras et al., 1995), the specific product molar concentrations are linear in time, as predicted by eq. 11. The rate coefficient for chain-end scission, k_s, can be obtained from the slope of the molar concentration of the specific product versus time. The dependence is consistent with eq. 12 when $k_{he} \ll k_{de} C$, which relates the chain-end scission rate coefficient to the H-donor concentration. The prediction of the continuous-kinetics model are thus consistent with the different observations of the H-donor effect on polymer decomposition.

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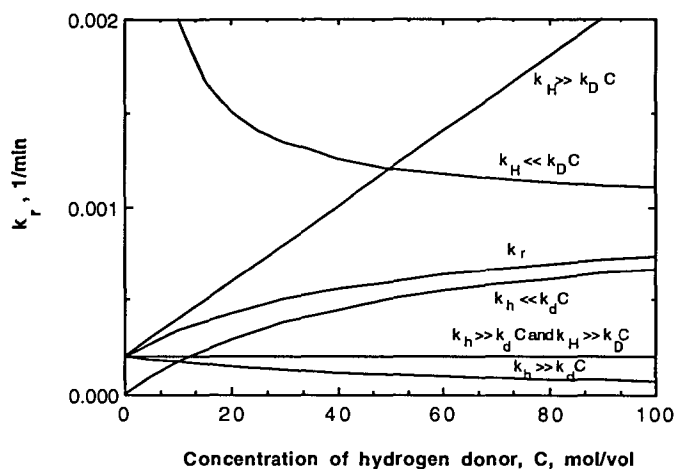
Figure 1. Plot of the rate coefficient of random chain scission, k_r, versus H-donor concentration, C, to show the different effects of the H-donor concentration and rate parameters (eq. 5).
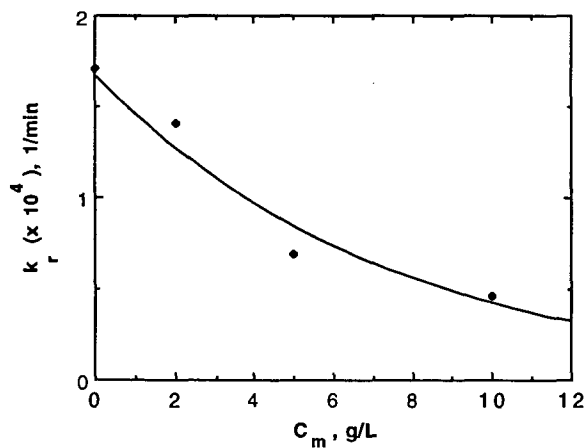
Figure 2. Effect of hydrogen donor (6-hydroxy tetralin) mass concentration, C_m, on the rate coefficient of random chain scission, k_r, of polystyrene at 275 C.